May 2003 • NREL/CP-520-33616

Conference Paper

Does Network Geometry Influence the Electron Transport Dynamics in Mesoporous Nanoparticle Solar Cells?

A.J. Frank, K.D. Benkstein, N. Kopidakis, and J. van de Lagemaat

Presented at the National Center for Photovoltaics and Solar Program Review Meeting
Denver, Colorado
March 24-26, 2003

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Does Network Geometry Influence the Electron Transport Dynamics in Mesoporous Nanoparticle Solar Cells?

A. J. Frank, K. D. Benkstein, N. Kopidakis, and J. van de Lagemaat
National Renewable Energy Laboratory
Golden, CO 80401

ABSTRACT

A major objective of our research is to define and solve the problems that limit the efficiency and commercial viability of solar cells based on dye-sensitized nanocrystalline TiO_2. Toward this end, we are currently elucidating the factors that govern charge transport and the loss mechanisms in mesoporous nanoparticle films of TiO_2. In this paper, we describe the first experimental evidence that the network geometry strongly influences electron transport and the first application of percolation theory to dye-sensitized solar cells.

1. Introduction

Dye-sensitized solar cells (DSSCs) are regarded as a viable economical alternative to inorganic photovoltaic cells owing to their moderately high efficiency (10.4% at AM 1.5) and potential low production costs. Despite their commercial promise, a number of important scientific issues that determine their performance are not well understood. One elusive issue is the elucidation of the principal factors that limit transport through the mesoporous films. Under normal solar intensities, the average time for the collection of photoinjected electrons in the nanoparticle films is in the millisecond-second domain, which is several orders of magnitude slower than the transport times for single-crystal TiO_2. We have shown that the slow collection time can be described quantitatively in terms of trap-limited transport [1]. Computer simulations, based on a random-walk approach and the assumption of an exponential distribution of trap depths, reproduce fully photocurrent transient data under the normal working conditions of DSSCs [1]. Until now, it has been assumed in the modeling of electron transport that network topology has no influence on it. Electrons are presumed to diffuse in three dimensions, restricted only by the macroscopic dimensions of the film and electrostatic interaction with the electrolyte (ambipolar diffusion [2]). In this paper, we discuss a recent study [3]. This study presents the first evidence that the network geometry strongly influences electron transport in mesoporous nanoparticle TiO_2 films and describes the first application of percolation theory to DSSCs [3].

2. Results and Discussion

Film characteristics. Figure 1 shows respective SEM images of 52%- and 71%-porous TiO_2 films composed of about 19-nm-diameter particles. A comparison of the two SEM images will show that the 71%-porous film has significantly more open space (dark areas) surrounding the clusters of particles than the 52%-porous film. In both cases, the pores constitute more than half of the volume of the film. It can also be seen in Fig. 1 that there is no apparent long-range order in the nanostructured films [4].

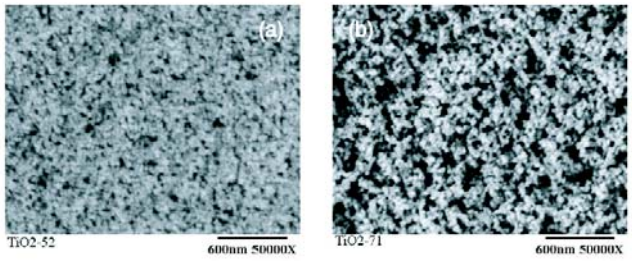

Figure 1. Plain-view SEM micrographs of (a) 52%- and (b) 71%-porous TiO_2 films.

Principal features of the physical structure of nanoparticle films can be described adequately by computer simulations [4]. Figure 2 shows the distribution of coordination numbers of the particles for film porosities ranging from 52% — 71%. At a film porosity of 58%, which is a typical film porosity used for the dye cell, about 10% of the particles have two neighbors, 25% of the particles have four neighbors, and less than 1% of the particles have eight neighbors. The average particle coordination number is 4.1. It can also be seen that as the porosity of the films increases from 52% - 71%, the distribution shifts from an emphasis on high coordination numbers to low ones. Furthermore, with increasing porosities, the fraction of single coordinated particles in a film increases dramatically. Such particles represent potential dead-ends in the electron transport pathways. An important implication of this discussion is that it is possible to manipulate the electron transport pathways through a nanoparticle network, making it more or less restrictive, by varying the film porosity.

Characterization of electron transport. The electron transport dynamics were characterized by transient photocurrent measurements. Figure 3 shows the dependence of the measured diffusion coefficient on the porosity of TiO_2 films for two electrolytes at a photocharge density of 10^{17} cm^{-3}. It is seen that the cation used in conjunction with iodide in the starting electrolyte influences the magnitude of the electron diffusion coefficient. The rate of transport is larger in the presence of the tetrabutylammonium cation-based electrolyte than in the case of the 1-hexyl-2,3-dimethylimidazolium cation-based electrolyte, suggesting that the two cations interact differently with the TiO_2 surface. It is also seen that as the porosity increases, electron transport becomes slower. The

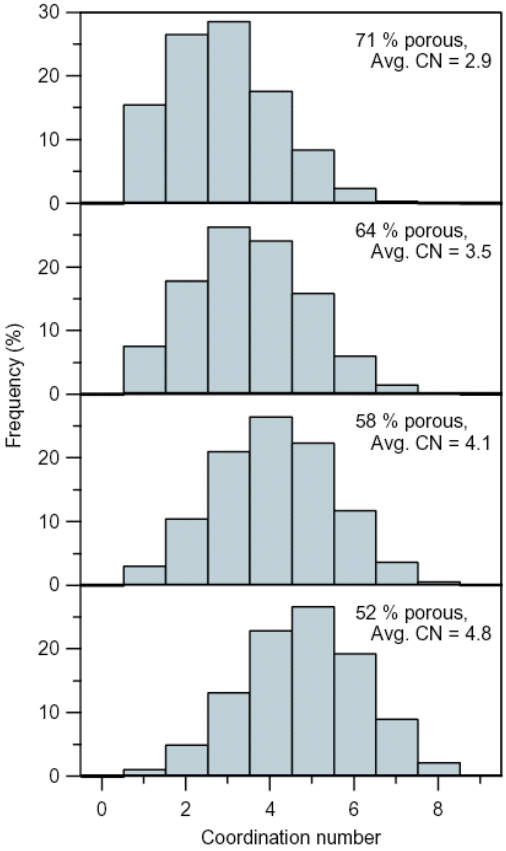

Figure 2. Dependence of the distribution of particle coordination numbers of simulated TiO_2 films on porosity.

solid lines correspond to the prediction of the percolation model — namely, the electron diffusion coefficient displays a power-law dependence on the film porosity with respect to a critical porosity (i.e., a percolation threshold). The very good correlation of the percolation model to the experimental data indicates that the percolation model describes very well the effect of porosity on electron transport. The same values of the parameters (critical porosity and a power-law exponent), which were obtained from fitting the percolation model to the random-walk simulations of electron transport on computer-generated particle networks, also describe the experimental data. The theoretical curves are scaled only in the y-direction to fit the experimental data, corresponding to different prefactors for the two-redox electrolytes. From the perspective of the percolation model, the experimental observation is consistent with the notion that the TiO_2 film is made up of a random particle network and that the rate of electron transport through it is strongly influenced by the density of interconnected electron pathways, i.e., by the distribution of particle coordination numbers at a given porosity. The consequence of increasing the film porosity is to increase the tortuousness, and thus the length, of the electron transport pathway.

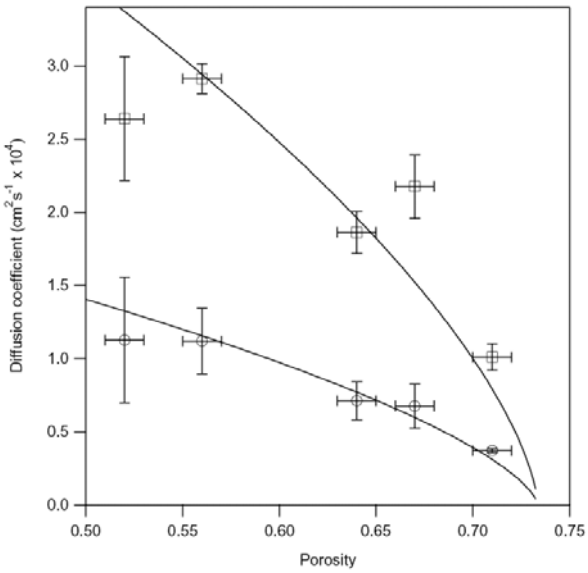

Figure 3. Dependence of the measured and predicted diffusion coefficient on the porosity at a photocharge density of 10^{17} cm^{-3} for two redox electrolytes in methoxypropriontirile: □ = 0.8 M tetrabutylammonium iodide and 0.05 M I_2 and ○ = 0.8 M 1-hexyl-2,3-dimethylimidazolium iodide and 0.05 M I_2. Solid lines are fits of the percolation model.

REFERENCES

[1] J. van de Lagemaat and A. J. Frank, J. Phys. Chem. B **105**, 11194 (2001).
[2] N. Kopidakis, E. A. Schiff, N.-G. Park, J. van de Lagemaat and A. J. Frank, J. Phys. Chem. B, J. Phys. Chem. B **104**, 3930 (2000).
[3] K. D. Benkstein, N. Kopidakis, J. van de Lagemaat, and A. J. Frank, submitted.
[4] J. van de Lagemaat, K. D. Benkstein, and A. J. Frank, J. Phys. Chem. B **105**, 12433 (2001).

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 2003	Conference Paper

4. TITLE AND SUBTITLE
Does Network Geometry Influence the Electron Transport Dynamics in Mesoporous Nanoparticle Solar Cells?

5. FUNDING NUMBERS
PVP3.2301

6. AUTHOR(S)
A.J. Frank, K.D. Benkstein, N. Kopidakis, and J. van de Lagemaat

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

8. PERFORMING ORGANIZATION REPORT NUMBER
NREL/CP-520-33616

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A major objective of our research is to define and solve the problems that limit the efficiency and commercial viability of solar cells based on dye-sensitized nanocrystalline TiO2. Toward this end, we are currently elucidating the factors that govern charge transport and the loss mechanisms in mesoporous nanoparticle films of TiO2. In this paper, we describe the first experimental evidence that the network geometry strongly influences electron transport and the first application of percolation theory to dye-sensitized solar cells.

14. SUBJECT TERMS
cells; electron transport; nanoscale materials; solar cells; titanium dioxide

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL